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POROSITY SWELLING AND TRANSMUTATION CONTRIBUTIONS TO CONDUCTIVITY CHANGES IN SOME NEUTRON-IRRADIATED COPPER ALLOYS

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Abstract

Fast-neutron irradiation of alloys for fusion-reactor applications produces bulk changes in density and composition via porosity swelling and transmutation which affect the dc volume electrical and thermal conductivities ($\sigma = 1/\rho_e$ and K). For the Cu materials of our study, neutron fluences of $2 \times 10^{26} n/m^2$ (E > 0.1 MeV) produced Ni and Zn weight increases of about 0.05 and 0.09%, respectively, and porosity swelling of 0-7%; ρ_e accordingly increased as much as 18%.

We also determined the individual ρ_e changes due to both swelling and transmutation via use of an appropriate mixing rule and of Matthiessen's law to unmask any residual effects present, e.g., phase or microstructural changes. For four materials -- two pure copper and two alumina-dispersion strengthened (ADS) alloys -- subtraction of these $\Delta\rho_e$'s from the irradiated values yielded or nearly yielded the respective control values. In contrast, the two precipitation-strengthened (PS) alloys studied, MZC and AMZIRC, had relatively large negative residues, apparently indicating effective radiation-induced conductivities.

Introduction

Recent magnetic fusion energy (MFE) concepts have included more compact reactor designs such as the compact reversed-field pinch reactor (CRFPR) being developed at Los Alamos. Such designs entail more intense first-wall loading by fast neutrons, heat, and other radiation. And for MFE reactors in general, thermal energy deposited in the first wall by eddy currents as well as radiation can lead to cyclic mechanical stresses via thermal gradients and thus to fatigue failure. Resistance to it is good when K and $1/\rho_e$ are high, as good heat conduction minimizes temperature gradients, and high electrical conductivity minimizes resistive heating.

At first, high-conductivity copper alloys may not seem as attractive for first-wall materials as alloys with high-temperature strength. However, an absence of magnetic metals in the alloy reduces the applied stresses (no magnetic domains) and hysteresis heating. Further, computer simulation predicts a peak copper first-wall temperature of 0.4 of the melting temperature T_m to arise in CRFPR design.[2] This is within the nominal strength-retention limit of 0.5 T_m. And, copper alloys strengthened by oxide dispersion or precipitates perform well. Taking S_y/ρ_e as a figure of merit (FOM) with S_y the room-temperature yield stress[2-3], then unirradiated annealed values for the Cu alloys featured here are nearly an order of magnitude higher than for Type 316 stainless steels or 6-4 Ti alloys.[3-5]

A major purpose of this study was thus to see how well electrical and thermal transport in Cu alloys "holds up" under irradiation by high fluence fast neutrons (E>0.1 MeV). Another was to use ρ_e

measurements to look for non-microscopical evidence of damage other than from void swelling or deleterious transmutation products.

Experimental Details

The elemental coppers used in this study were an oxygen-free high-conductivity (OFHC) type annealed after cold rolling, plus a high-purity (99.999%) MARZ copper initially in the cold-rolled condition. Two PS copper alloys, MZC and AMZIRC (both AMAX), were tested in a 90% cold-rolled and aged condition. Also, two ADS copper alloys, Al-20 and Al-60 (SCM Metal) with alumina contents of 0.2 and 0.6 wt.%, were 83% cold rolled, annealed, cold rolled again (by 70%), and re-annealed. Further details are reported elsewhere.[5-6]

The materials were cut from sheet stock and irradiated at 385°C as "matchstick" specimens $3\frac{1}{2}$ cm x $\frac{1}{2}$ to 1 mm^2 in the Experimental Breeder Reactor (EBR-II) at fluences of 0.4 and 2.0 x 10^{26} n/m^2 corresponding to damage levels of 3 and 15 dpa. Controls were annealed for the same temperature and concomitant time conditions.

Four-point measurements of dc electrical resistance were measured remotely on the "jig" shown in Fig. 1. A programmable current source connected to the specimen ends produced voltage "drops" measured by a nanovoltmeter placed across the 'knife-edge' contacts. "Steps" of different amplitudes and both polarities in the current sequence programmed minimized zero-offset and other errors in the voltage readings. Further details are included elsewhere.[6] Resistances were combined with cross sections calculated from densities measured via air and immersion weights of specimens to determine ρ_e. An analysis of variance was performed on data so that the statistical significance of small differences could be assessed to an overall 95% confidence level for the ensemble of tests performed for the binary or multiple comparison tests performed as well.

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Results: As-Measured Properties

Table 1 presents the results for control (C), low-fluence (L), and high-fluence (H) specimens. Typical standard errors for as-measured ρ_e are 0.006 μΩ-cm. The ρ_e's are converted to IACS conductivities via $\sigma(IACS) = 172.41/\rho_e$. The measurements agree well with tabulated values, e.g., 1.70 vs. 1.71 μΩ-cm for OFHC and 1.67 vs. 1.67 μΩ-cm for MARZ.[7] Thermal conductivity K was calculated via the Smith-Palmer relation[3-9] which incorporates the Wiedemann-Franz law for the electronic contribution and an empirical term b for the phonon contribution (b = 0.075 W/cm-K) assumed applicable here to irradiated as well as 'cold' Cu. The fractional changes in K equal [(b/K)-1] times those for ρ_e. No definite pattern in ρ_e vs. fluence is evident, but the results for $\delta\rho_e/\rho_e$ vs. fluence separate into three distinct groups: Pure, ADS, and PS copper, with the greatest changes occurring for the first. Yet MZC showed a decrease in ρ_e -- small but significant.

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Application of the Student-Newman-Keuls statistical test to the ρ_e's indicated that all fluence-related differences for fixed materials were significant except for C vs. L for MZC. Further, at fixed fluence within any of the three material groups (pure, ADS, or PS), only two of the nine ρ_e differences were not significant: OFHC-H vs. MARZ-H and MZC-H vs. AMZIRC-H.

Results: Porosity and Transmutation Contributions

The as-measured values of ρ_e for irradiated copper can be recalculated to remove effects due to porosity swelling and transmutation products. The differences between the resulting doubly corrected values and the corresponding control values yield ρ_e 'residues' possibly due to some other mechanism(s).

First considered is a correction for porosity swelling of material assumed to be initially fully dense (FD). For simplicity, only two, homogeneous phases are considered: The FD copper and interspersed non-conducting pores. Pore dimensions are assumed larger than the electron mean free path Λ so that the resistance increment due to electron scattering is independent of pore size under conditions of fixed total porosity of volume fraction v. ($\Lambda \approx 300 Å$ for pure Cu at 300 K.[10]) Then an appropriate mixing rule (due to Maxwell) for ρ_e is:

$$\rho_e' = [(1 + \tfrac{1}{2} v)/(1-v)](\rho_e)_{FD} \qquad (1)$$

where ρ_e' and $(\rho_e)_{FD}$ are the mixture and FD values.

The porosity is assumed randomly distributed in the FD Cu as randomly-sized spheres.[11] The mixture ρ_e' is identified with the as-measured ρ_e. Furthermore, v equals $(\rho_{FD}-\rho')/\rho'$ in terms of the FD and as-measured mass densities. If ρ_{FD} is the density of the control, then $(\rho_e)_{FD}$ for the radioactive 'matrix' of the material can be calculated; results for the "H" case are tabulated in Table 2. Most of the radiation-induced changes in ρ_e for pure copper are due to their swelling of 7%. Little change occurs for Al-20 and Al-60; none occurs for MZC, which did not swell. To the 95% confidence level, neither the density change (- 0.05 g/cm^3) nor the difference $\rho_e' - (\rho_e)_{FD}$ (0.01 μΩ-cm) for Al-20 was significant.

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Estimated also were the increases in ρ_e due to the principal transmutation elements expected, Ni and Zn.[12] Chemical analysis of both C and H specimens indicated Ni and Zn increases of 0.053 and 0.087 wt.%, respectively. These small amounts are assumed to be dissolved in the Cu so that the concentration rates, β, of increase of ρ_e in Cu-Ni and Cu-Zn binary alloys could be used in accordance with Nordheim's rule; they are 1.25 and 0.32 μΩ-cm/at.%, respectively.[13] In other words, the temperature-independent impurity-sensitive term in Matthiessen's expression for ρ_e is taken to be linear in concentration and additive with impurity type in 'dilute' alloys. The corresponding total increase $\beta_{Ni}C_{Ni} + \beta_{Zn}C_{Zn}$ expected in ρ_e was calculated and subtracted from the FD values (C = at.%). See Table 2 for ρ_e without void swelling or transmutation effects, i.e., for the sum of the control value $(\rho_e)_C$ and a residue term. The residue is essentially zero for the elemental coppers and the ADS alloys; microstructural changes have apparently little or no effect on ρ_e. This is consistent with the known effects in Cu of point and line defects.

For example, the ρ_e increase measured at 4.5 K for Frenkel-pair production by fast neutrons is expected to saturate at 0.33-μΩ (which would anneal out at the 658 K of the present study).[14] A value for the ρ_e increase in Cu due to dislocations is 1.3 N x 10^{-13} μΩ-cm^3, with N the dislocation density in cm^{-2} units.[15] Assuming a residue of + 0.1 μΩ-cm (Table 2) leads to a high N value of 7.7 x 10^{11}cm^{-2}, unlikely to remain given the annealing conditions of 385°C (for 245 days) pertinent to our study.

For MZC and AMZIRC the residues are much greater. A phenomenon not soley related to swelling, transmutation, or thermal annealing may produce a small decrease in ρ_e of both these alloys. Such 'radiation-induced conductivities' were reported decades ago on Cu alloyed with aluminum[16] and zinc.[17] A saturating, diffusion-controlled solid-state reaction mechanism was invoked for the ρ_e decreases, an enhanced diffusion supposedly resulting from extra defects produced during sample preparation.[16] An alternative and opposing view applied to α-brass is that changes in short-rang order govern the ρ_e decreases.[17] In either case, the neutrons may disturb both the rate and the final state to which non-equilibrium alloys relax.[6]

Discussion and Conclusions

The fast-neutron irradiation study of Cu closest in character to ours was done on Cu alloys in the MOTA Fast Flux Test Reactor (FFTF) to a fluence of 2.5×10^{26} n/m^2 at 450°C and a damage level of 16 dpa.[18] The one material the same in both studies was the annealed 99.999% pure copper (MARZ): The as-measured ρ_e's are nearly identical in both. However, for the only 'common' alloys MZC and Al-25, the substantial differences in details on cold-working, aging, alloy composition, and irradiation temperature hinder meaningful comparisons. In particular, the FFTF irradiated-vs.-control differences in ρ_e in principle contain specimen-annealing as well as fluence-related differences, as the control ρ_e's were apparently measured on alloys in an 'as-received' condition.

The initiation of damage resulting from EBR-II is much less than expected from the 14 MeV neutron flux of a fusion reactor. For example, a 16 dpa/yr peak would result in Cu for 1 $MW\text{-}yr/m^2$ of 14 MeV neutrons; a full power year at the first-wall in CRFPR would yield 318 dpa.[19] The actual damage depends on the self-healing response of the alloy. Thus, stability of ρ_e under radiation stress is in practice more important than the initial 'cold' value of ρ_e. Further, the average atomic weights, mix, and yield of transmuted Ni and Zn would differ; e.g., our wt.% ratio of Zn to Ni is 1.6 but for CRFPR is 0.56.[1] Also, 1 $MW\text{-}yr/m^2$ of 14 MeV neutrons increase ρ_e by 0.35 $\mu\Omega$-cm (assuming atomic dispersal of the Ni and Zn),[1,13] in contrast to the 0.10 $\mu\Omega$-cm of our study.

Potential for ρ_e characterization of microstructure exists in the sensitivity of electron scattering to atomic and spin distributions in metals, and thus to clustering, kinetics of short- and long-range ordering, and phase separation.[20] Also, the Maxwell model used here to estimate porosity effects on ρ_e can, in its full expression (i.e., with $1/\rho_e > 0$ for the spheres), be applied to the ρ_e residue to 'track' the radiation-induced redistribution of precipitates in PS alloys.[11] This is suggested by the recent use of the Maxwell model and ρ_e measurements to study crystallization kinetics in amorphous Pd-Si metallic glasses.[21] However, a note of caution is in order here: None of the residue differences from zero achieved statistical significance *per se* for the Type I error rate (0.05) chosen in our analysis. While we have presented some evidence for their physical significance, the use of ρ_e residues for indirect characterization of microstructure requires increased measurement precision and statistical sample size. The standard deviations associated with the residues were typically an order of magnitude larger than for the as-measured ρ_e's because of multiple propagation of errors resulting from use of density data in Eq. (1).

Good performance of ρ_e and K *per se* satisfies only partially the total operating requirement of a first-wall alloy, as indicated by our reference to the FOM S_y/ρ_e for both mechanical and physical properties. When this is done it is the ADS rather than PS irradiated alloys that offer the more promise as engineering solutions to the first-wall problem.[6,22] In general, an objective basis for materials selection has been lacking in the past because FOM criteria have not been systematically applied to *irradiated* alloys.

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Fig. 1. Specimen holder for 4-point measurements of electrical resistance. Contact was maintained by weights guided onto specimen via the guide posts shown.

Table 1. Conductivities for copper alloys irradiated to two fluences by fast neutrons

Copper Material	Neutron Fluence	Electrical Properties: As Measured σ(IACS) (%)	Electrical Properties: As Measured ρ_e ($\mu\Omega$-cm)	Electrical Properties: $\delta\rho_e/\rho_e$ (%)	Thermal Conductivity (W/K-cm)
OFHC	C	101	1.70	0.0	4.2
	L	95	1.82	6.9	3.9
	H	87	1.98	16.6	3.6
MARZ	C	103	1.67	0.0	4.3
	L	97	1.78	6.7	4.0
	H	87	1.98	18.4	3.6
Al-20[1]	C	94	1.84	0.0	3.9
	L	90	1.91	3.9	3.7
	H	88	1.95	6.1	3.7
Al-60[1]	C	87	1.99	0.0	3.6
	L	83	2.08	4.3	3.4
	H	81	2.13	7.1	3.4
MZC	C	89	1.93	0.0	3.7
	L	89	1.94	0.6	3.7
	H	92	1.88	-2.4	3.8
AMZIRC	C	97	1.77	0.0	4.0
	L	96	1.80	1.7	4.0
	H	92	1.87	5.2	3.8

[1] With a nominal 5% cladding of OFHC Cu on each side.

Note: Neutron fluence symbols explained in text (H > L > C).

Table 2. Resistivities corrected for porosity swelling and transmutation products

Copper Material	Neutron Fluence	Density (g/cm^3)	DC Volume Resistivity ($\mu\Omega$-cm): As-Measured	Corr. for Increases Due to Porosity	Corr. for Increases Due to + Transm.	Residue
OFHC	C	8.87	1.70	0.00	0.00	0.00
	H	8.29	1.98	1.78	1.68	- 0.02
MARZ	C	8.88	1.67	0.00	0.00	0.00
	H	8.27	1.98	1.77	1.67	0.00
Al-20	C	8.76	1.84	0.00	0.00	0.00
	H	8.71	1.95	1.94	1.84	0.00
Al-60	C	8.77	1.99	0.00	0.00	0.00
	H	8.68	2.13	2.10	2.00	+ 0.01
MZC	C	8.88	1.93	0.00	0.00	0.00
	H	8.88	1.83	1.88	1.78	- 0.14
AMZIRC	C	8.92	1.77	0.00	0.00	0.00
	H	8.60	1.87	1.76	1.66	- 0.11